STUDY OF RESORCINOL PRODUCTION

BY

J. M. BERNSTEIN

E. G. VOGT

ARMOUR INSTITUTE OF TECHNOLOGY

1920

667.2
B 46

Illinois Institute
of Technology
UNIVERSITY LIBRARIES

AT 528
Bernstein, J. M.
A study of resorcinol
production

For Use In Library Only

Digitized by the Internet Archive
in 2009 with funding from
CARLI: Consortium of Academic and Research Libraries in Illinois

http://www.archive.org/details/studyofresorcino00bern

A Study of Resorcinol Production

A THESIS

PRESENTED BY

JOSEPH M. BERNSTEIN AND EMIL G. VOGT

TO THE

PRESIDENT AND FACULTY

OF

ARMOUR INSTITUTE OF TECHNOLOGY

FOR THE DEGREE OF

BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

MAY 27, 1920

APPROVED:

A. McCormack
Professor of Chemical Engineering

Dean of Engineering Studies

Dean of Cultural Studies

ILLINOIS INSTITUTE OF TECHNOLOGY
PAUL V. GALVIN LIBRARY
35 WEST 33RD STREET
CHICAGO, IL 60616

TABLE OF CONTENTS.

	Page.
Introduction	1
Theoretical and Practial Considerations	8
Calculations	16
Experimental Work	24
Discussion of Graphs	58
References	64
Conclusions	69

29116

Introduction.

It can be said without fear of succdssful contradiction, that our sudden entry in the "World War", although an evil in itself, was not without its redeeming features. Our absolute dependence upon Germany for our chemicals more particularly the dyestuff chemicals, was a matter that was only too well known. Therefore, when Germany's market was so suddenly closed to our insistent buyers, a serious crisis was reached which needed immediate attention. The existing stocks of the more staple chemicals were not very great, and then sudden cessation of further additions to them, boosted their prices to previously unknown and undreamed of heights. This state of affairs is very aptly shown by the chart for the price variations of resorcinol during a period of four years which is given on another page.

Germany's method of ruthless trade warfare never did allow America to become a successful trade competitor in the chemical industry. In spite of protective tariffs and other helpful measures, America was never able to compete successfully with

Germany's well organized and government favored industry. It can easily be seen that conditions were in a sad mess when Germany's market was suddenly closed to us. Following this, an appeal was made to the American chemist and chemical engineer. How well this appeal has been answered is self-evident to those who have watched the progress of the chemical industries in the United States during the past five years.

These problems which so suddenly confronted our chemists and chemical engineers in the early years of the great war, were not solved overnight. It has been a hard and painstaking task, and the success that has attended the chemists and chemical engineers is not only due to their perseverance and labor, but a great measure of deserving praise must also go to the men who were willing to assume an initial loss and still keep on financing the workers. The authors, at a lecture on dyestuffs in 1918, were shown a jar containing two pounds of a fast blue dye which was the product of twenty thousand dollars worth of endeavor and labor, and the speaker made the remark that it would cost many times

the initial $20,000 before the product could be made on a commercial scale.

Many of these problems have been solved satisfactorily. There are other problems which have not been fully solved and which will require many years of work. Then again, there are other problems which appear on the surface as if they were fully solved but which, upon closer investigation will be shown to permit of a good many refinements and economies in their method of execution so that the cost of manufacture can be brought down considerably. It is one of these latter problems that has attracted the authors' attention and in the following thesis, an attempt has been made to apply a few refinements to the preparation of resorcinol. In reality it is a study of resorcinol production, as the title of the thesis indicates.

Resorcinol is a definite chemical compound, being the meta- di- hydroxi derivative of benzene and its formula is $C_6 H_4 (OH)_2$ m. It finds its great use and importance as a pharmaceutical preparation and as an intermediate product in the manufacture of "coal-tar" dyes. It is a remarkable fact that resorcinol

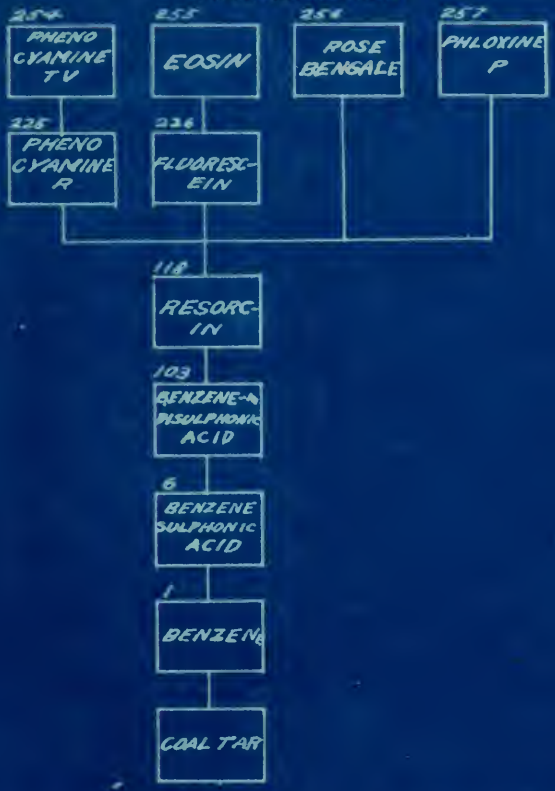
can be prepared from ortho, meta, or para brom-phenol and from meta or para benzene-disulfonic acid. It can also be prepared from m.-phenol-sulfonic acid, m-iodo-phenol, p-chlor-benzene-sulfonic acid and from many resins by an alkali fusion.

Resorcinol crystallizes in rhombic plates from alcohol, ether, and water and in needles from benzene. It is very soluble in ethyl alcohol, amyl alcohol, ether, and water; and it is insoluble in carbon disulfid and chloroform. Upon exposure to the air, the crystals become brown. Ferric chlorid colors an aqueous solution of resorcinol a dark violet color which disappears upon the addition of sodium acetate: It reduces boiling ammoniacal $AgNO_3$ and boiling Fehlings' solutions. It acts therapeutically like phenol, only more mildly. Its reactions are characteristic of phenol.

The accompanying chart prepared by Thomas H. Norton entitled "Derivation of Leading Coal-Tar Colors, Adapted from the 'Coal-Tar Tree' of H. Von Brunck, director of the Badische Aniline and Soda Fabrik" and found in the supplement to the issue of the Oil, Paint

FIG. 1

DERIVATION OF LEADING COAL TAR COLORS
ADAPTED FROM THE "COAL-TAR TREE" OF
H. von BRUNCK

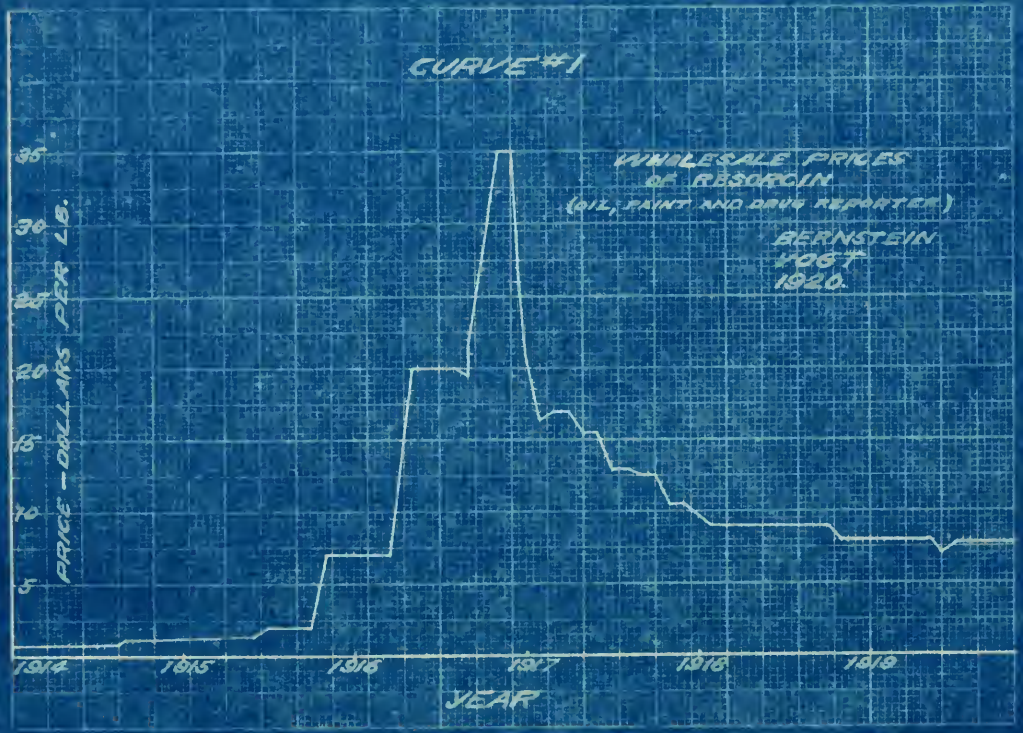


THE RESORCIN BRANCH OF THE IMPORTANT
COAL TAR DYES

BERNSTEIN
VOGT
1920

and Drug Reporter, October 2, 1916, shows the relation of resorcinol to some other coal tar products. A few other dyes for which it is used are: Fast green (dinitroresorcinol), the dyes derived from fluorescein, Sudan G, Resorcine yellow, Acid alizarin garnet R, Resorcine brown, Fast brown, Pyramidol brown BG and T, Congo 4R, Isodiphenyl black R, Coomassie union blacks, Congo brown G, (Direct brown GR) Congo brown R, Azocorinth and Hessian brown BBN.

The present price of resorcinol is about eight times that of pre-war days when the common wholesale prices of the crystals was $0.80 to $0.85 a pound. The present market quotations have been fairly constant for a time at $6.00 a pound. No apparent reason can be found for the maintenance of such a high price and that is one reason why the problem of the manufacture of this chemical cannot be considered to be completely solved. In the accompanying curve No.1, there is shown a record of the change in the wholesale market price of this chemical for the past six years, starting with Germany's entry into the war.


CURVE #1
WHOLESALE PRICES OF RESORCIN
(OIL, PAINT AND DRUG REPORTER)
BERNSTEIN
VOGT
1920.
PRICE - DOLLARS PER LB.
35
30
25
20
15
10
5
1914
1915
1916
1917
1918
1919
YEAR

The remarkable changes shown in the market price of this item reached its maximum in the last couple of months of 1916. The first advertisement for its sale by an American manufacturer appeared in the Oil, Paint, and Drug Reporter about September 1916, when the market price had reached about $25.00 a pound. The market continued to advance until it reached $35.00 a pound in the latter part of the same year. With the enormous profits at the above market price as an incentive for the chemical manufacturer's entry into this field, competition gradually increased and slowly caused a continual decline in the market price until the present quotation of $6.00 a pound was reached. In the authors' minds, there is no logical explanation for the fact that resorcinol sells for a price fifty times greater than that of phenol which at present is quoted for $0.12 a pound. In the manufacture of both of these, the same operations are followed, the only difference being that higher concentrations of reagents and higher temperatures are utilized in the preparation of resorcinol and different solvents are used for extraction.

The authors attacked this problem with the idea that the present method of preparing resorcinol could not be improved upon, except in one or two minor details. Bearing in mind the fact that the extraction of the resorcinol from the neutralized solution with ether or amyl alcohol is too expensive and entails too great a loss of ether; the authors will attempt to show in this thesis that a more feasible, practical and economical way to extract the resorcinol consists of extraction with alcohol from the salts which have been brought down to dryness. The reason for this is very apparent when it is noted that Cain, in his "Manufacture of Intermediate Products for Dyes" page 127, says that "for each 5 kilos of resorcinol, 1 kilo of ether, or 1 per cent of the amount used is lost." In actual practice this loss runs higher.

For their kind and helpful suggestions, the authors wish to express their deep appreciation to their friends, especially Professor McCormack whose practical suggestions were of great assistance: We are also indebted to D. E. Cable, and J.I. Prest of the class of 1918 whose thesis we have freely consulted.

Theoretical and Practical Considerations.

In the preparation of the sodium salt of m- benzene-disulfonic acid, and in the subsequent fusion with caustic alkali, the authors, having had no practical, commercial experience, applied the methods and general outlines given in the chemical literature.

When benzene is heated with strong sulfuric acid, either the mono- or di-sulfonic acid, or a mixture of the two, is formed, depending upon the concentration of acid used and the temperature of sulfonation. When a 64° Be' acid is heated with benzene at a temperature just below the boiling point of benzene, the mono-sulfonic acid is the only product of the reaction after seven or eight hours heating. The di-sulfonic acid may be produced by using fuming sulfuric acid with the benzene, first at the low temperature for two or three hours, then at a high temperature, about 250°C. The sulfonation at the two different temperatures can either be carried out in one operation, or in two operations.

According to Cain, "Intermediate Products for Dyes", page 126 in the preparation of benzene-m- disulfonic acid, "Ninety kilos of fuming sulfuric acid are placed in a cast iron pan fitted with a stirrer and reflux condenser made of a leaden coil, and 24 kilos of benzene are added in a thin stream thru the condenser. The temperature gradually rises to the boiling point of benzene, and after two to three hours, the latter is converted into the monosulfonic acid. The reflux condenser is then shut off and the pan is connected with an ordinary condenser. The temperature is now raised gradually to 275°, and water and a little benzene distil over. After heating for about twenty minutes at this temperature, the mass is allowed to cool, and is blown into 2000 litres of water."

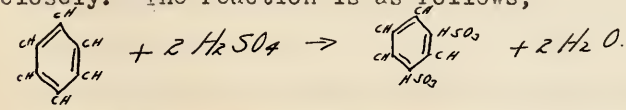
According to Behrend and Mertelsmann (Annalen, 1911,378,352) the sulfonation of benzene by pure concentrated H_2SO_4 at 240° - 250° results almost exclusively in the formation of the m- disulfonic acid, less than one per cent of the para isomeride being produced after one and one half hours heating. The addition of a little mercury causes the formation

of the m- and p- acids in the proportion of 2:1; ferrous sulfate acts similarly about 10% of the para-di-sulfonic acid being produced.

Polak (Rec. trav. chim., 1910,14,416) reports that the sulfonation of benzene sulfonic acid, either with fuming H_2SO_4 or with 98% H_2SO_4, results in complete sulfonation to di-sulfonic acid at 209° while at 233°, some tri-sulfonic acid is formed.

Lamberts (G.P. 113784) mixes benzene with five times its weight of sodium hydrogen disulfate $NaH_3(SO_4)_2$ (prepared by heating sodium bisulfate with 60°Be' H_2SO_4) and heats the mixture gradually to 200° where it is kept for some time. Upon dilution and treatment with milk of lime, the filtrate consists of a solution of the sodium salt of the disulfonic acid.

In our work, we followed Cain's method fairly closely. The reaction is as follows,

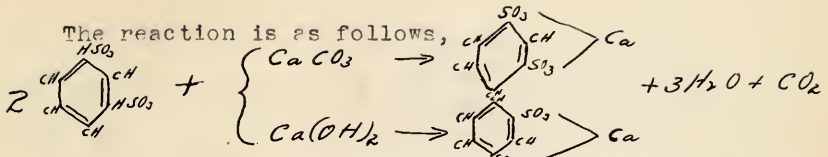


In the preparation of the di-sulfonic acid, the entering acid groups follow the general substitution rule and the main product of the reaction is the

meta compound.

The soluble di-sulfonic acid is now separated from the excess sulfuric acid. This is accomplished by precipitating the excess sulfuric acid with milk of lime, filter off and wash the precipitated calcium sulfate. The separation is possible because of the fact that calcium and other base metals like barium and lead form soluble salts of the di-sulfonic acid, and insoluble sulfates. Commercially, the conversion to the calcium salt, and its subsequent separation from the insoluble sulfate is accomplished by blowing milk of lime into a solution of the sulfonation mixture contained in a lead lined tub fitted with an agitator and a perforated lead steam coil, until the mass is very nearly neutral. Complete neutralization is then effected by adding precipitated $CaCO_3$ which is obtained from the next operation. The neutralized mixture is then filtered, and the $CaSO_4$ is washed thoroughly; the filtrate containing the soluble calcium- m-benzene-di-sulfonate is then ready for conversion to the sodium salt.

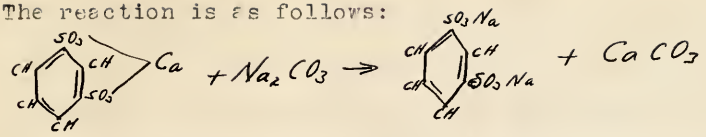
The reaction is as follows,



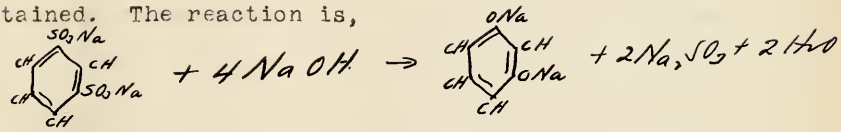
Dennis (U.S.P. 1227252) proposes to treat a mixture of benzene disulfonic acid and H_2SO_4, with benzene which dissolves the sulfonic acid but not the H_2SO_4 and then treats the solution with a suitable compound to form a salt of the sulfonic acid which is relatively insoluble in the benzene.

In the conversion of the calcium salt to the sodium- salt, the filtrate from the preceding operation, is stirred, and a solution of Na_2CO_3 is gradually added until a filtered sample gives no precipitate of $CaCO_3$ upon the addition of a little Na_2CO_3. It should also not give a precipitate with a soluble calcium salt, showing that the liquid has been exactly neutralized. The precipitated $CaCO_3$ is filtered off, and thoroughly washed to free it from the sodium salt; it is then used in the preceding operation for neutralization. The solution containing the sodium-salt is then evaporated, and finally, thoroughly dried under a vacuum. The dried salt, known as the "silver salt", is now ready for fusion with caustic NaOH.

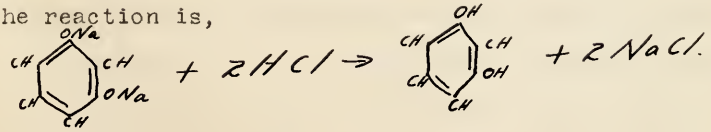
The reaction is as follows:



In the fusion with caustic alkali, a considerable excess of NaOH is used. The reaction is conducted in a cast iron kettle with means for continuous, mechanical agitation, while the fusion mass is kept at about 280° for 7 to 8 hours. As a result of this fusion, the sulfo radicals are removed and sodium- m-di-phenoxid is the product obtained. The reaction is,



By acidifying the solution of the fusion mass to the neutral point, and then by the subsequent proper extraction, the resorcinol is obtained. By this acidification the Na atoms are replaced by the H atoms. The reaction is,



There are two common ways of making the caustic fusion; first, in an open kettle; and second, in an autoclave. The first is the more common method, and

and is described to the greatest extent in the literature. The second method, however, is coming into greater use right along. A. H. Ney and D. J. Van Marle in their article on "The Processes of the Organic Chemical Industry Used in the Manufacture of Intermediate Products," published in the Metallurgical and Chemical Engineering Magazine February 15, 1917, say, "In the fusion with caustic soda, the sulfonic acid probably first goes over into an ester of sulfurous acid which subsequently is decomposed into a phenolic body and sodium sulfite. This reaction takes place only at a high temperature, which makes it necessary to use an excess of caustic to keep the mixture in a liquid state at this temperature, but as many organic compounds are easily oxidized in the presence of caustic soda at a high temperature, ... a considerable amount of material is lost through oxidation and leaves the yield much to be desired. . . . . This can often be improved by carrying out the caustic fusion with water in autoclaves under pressure, which allows the amount of caustic soda to be cut down materially and prevents oxidation. The disadvantage of using autoclaves is

their limited capacity and the long time required for their operation. . . . . In the case of di- and tri- sulfonic acids, however, a much larger excess of caustic soda has to be used (than in the case of the mono-sulfonic acid) and here generally, the use of autoclaves will be preferred. . . . . In these higher sulfonic acids, the sulfonic acid groups are not all at once replaced; benzene- m-disulfonic acid, for instance first being converted into phenol-m-sulfonic acid, then into meta-dioxybenzol or resorcinol. . . . . .

Caustic fusions are carried out either in open cast iron kettles, in which the caustic soda is fused and the sodium sulfonate gradually added, or in autoclaves under pressure. . . . . Both autoclaves and fusion kettles are provided with an agitator and are placed in a furnace which is heated by oil or gas as the temperature to which the mixture is heated is often about 300°C."

Calculations.

In our experimental work, it was desired to sulfonate with a 100.9% fuming H_2SO_4 which is equivalent to 4% free SO_3. The only acids obtainable in the laboratory were those of 104.5% fuming H_2SO_4 and 96% H_2SO_4. The 104.5% H_2SO_4 was therefore diluted with the 96% acid according to the following equation,

$$x = \frac{1(104.5 - 100.9)}{(100.9 - 96)} = \frac{3.6}{3.4} = \frac{3}{4}$$

in which x equals grams of 100.9% acid; Therefore, for every gram of 104.5% H_2SO_4, $\frac{3}{4}$ gram of 96% H_2SO_4 was added, and this ratio gave the desired 100.9% H_2SO_4.

Sp. G. of 100.9% H_2SO_4 = 1.869

Sp. G. of 104.5% H_2SO_4 = 1.9275

Sp. G. of 96% H_2SO_4 = 1.84

1000 grams of 104.5% acid equals $\frac{1000}{1.9275}$ or 518cc.
750 grams of 96% acid equals $\frac{750}{1.84}$ or 408cc. Therefore, 518cc of the 104.5% acid added to 408cc of the 96% acid gave 926cc of the 100.9% acid which was used in the sulfonations. When further quantities of acid were desired, the above ratio was followed.

$$\underset{\substack{78\\100}}{C_6H_6} + \underset{98}{H_2SO_4} \rightarrow C_6H_5SO_3H + \underset{18}{H_2O}$$
$$\qquad\qquad\quad x \qquad\qquad\qquad\quad y$$

$\frac{78}{100} = \frac{98}{x}$ $x = 125.8$

∴ 125.8 grams of 100% H_2SO_4 are required to sulfonate 100 grams of benzene to mono-sulfonic acid. But 4% fuming acid was used, and for every 100 grams of 4% fuming acid there are 4 grams of free SO_3.

$$\underset{\substack{80\\4}}{1\ SO_3} = \underset{98}{1H_2SO_4}$$
$$\qquad\quad x$$

$\frac{80}{4} = \frac{98}{x}$ $x = 4.9$ grams.

∴ 4 grams of SO_3 = 4.9 grams of 100% H_2SO_4. Therefore, 100 grams of 4% fuming are equivalent to 100.9 grams of 100% H_2SO_4. 125.8 grams of 100% acid = $\frac{100}{100.9}$ x 125.8 or 125 grams of 4% fuming acid. Therefore, for sulfonation to the mono-sulfonic acid, 125 grams of the 4% fuming acid are required.

$\frac{78}{100} = \frac{18}{y}$ $y = 23.1$

Therefore, for sulfonation to the mono-sulfonic acid, 23.1 grams of water are liberated.

To determine the amount of acid that remains after complete sulfonation, the following calculations are required; 100 grams of benzene to disulfonic acid liberates 46.2 grams water. 100 grams of benzene for this reaction

requires 250 grams of 4% fuming acid. Assume the use of 350 grams of 4% acid.

350 - 250 = 100 grams of 4% fuming

.04 x 100 = 4 grams of SO_3

100 - 4 = 96 grams of 100% H_2SO_4

$$\underset{\substack{18\\ x}}{H_2O} + \underset{80}{SO_3} \longrightarrow \underset{98}{H_2SO_4}$$
$$\quad\quad\; 4$$

x = 0.9 grams of water required to combine with the free SO_3.

46.2 - 0.9 = 45.3 grams of water left to combine with the 100% H_2SO_4. The 4 grams of water plus the 0.9 grams of SO_3 combine to give 4.9 grams of 100% H_2SO_4. Total 100% H_2SO_4 equals 96+4.9 = 100.9 grams. 100.9 grams of 100% H_2SO_4 plus 45.3 grams H_2O equals 146.2 grams hydrated H_2SO_4. Percent H_2SO_4 by weight = $\frac{100.9}{146.2}$ = 69% which is equivalent to a 54.5°Re' acid = Sp. G. 1.604.

In the preparation of the disulfonic acid, there are required 2x125, or 250grams of 4% fuming acid, or 251.6 grams of 100% H_2SO_4. In this preparation, 46.2 grams of water are liberated. These 46.2 grams of water will be absorbed by the acid, but it must leave the acid still strong enough to complete the sulfonation.

The amount of benzene-di-sulfonic acid theoretically possible from 100 grams of benzene is shown by the following reaction,

$$\underset{78}{C_6H_6} + 2H_2SO_4 \rightarrow C_6H_4 \underset{238}{(SO_3H)_2} + 2H_2O.$$
$$100 \qquad\qquad x$$

x = 305 grams benzene-di-sulfonic acid which may be produced.

The amount of calcium-benzene-di-sulfonate which is theoretically possible by conversion of the previous amount of di-sulfonic acid with milk of lime, is shown by the following reaction,

$$\underset{238}{C_6H_4(HSO_3)_2} + \underset{56}{CaO} \rightarrow \underset{276}{C_6H_4(SO_3)_2Ca} + H_2O$$
$$305 \qquad x \qquad\qquad y$$

x = 71.7 grams of CaO which are required to neutralize the benzene-di-sulfonic acid from 100 grams of benzene. The excess acid remaining after complete sulfonation equals 100.9 grams of 100% acid.

$$\underset{98}{H_2SO_4} + \underset{56}{CaO} \rightarrow CaSO_4 + H_2O$$
$$100.9 \qquad x$$

x = 57.7 grams CaO required to neutralize the excess acid. Therefore, the total amount of lime required for neutralization and conversion to the calcium salt is equal to 71.7 + 57.7 = 129.4 grams. Allowing a 10% excess, the amount of lime that should be used equals 142 grams on

the basis of using 100 grams of benzene.

$\frac{238}{305} = \frac{276}{y}$ $\quad y = 354$

Therefore, starting with 100 grams of benzene, 354 grams of calcium-benzene-disulfonate are produced after conversion.

Theoretically, 354 grams of the calcium salt are derived from 100 grams of benzene. In the conversion of the calcium salt to the sodium salt, the following calculations show the amount of soda ash required, and the amount of sodium salt derived.

$$\underset{276}{C_6H_4(SO_3)_2}\ Ca + \underset{106}{Na_2CO_3} \longrightarrow \underset{282}{C_6H_4(SO_3Na)_2} + CaCO_3$$

$$\begin{matrix} 354 & x & y \end{matrix}$$

$x = 136 \qquad y = 362$

Therefore, 136 grams of soda ash are required for complete conversion to the sodium salt, and 362 grams of the sodium-benzene-disulfonate are theoretically derived.

To show the amount of NaOH that theory requires to react completely with 362 grams of sodium salt which is the theoretical product from 100 grams of benzene, the following calculations are necessary.

$$\underset{282}{C_6H_4(SO_3Na)_2} + \underset{160}{4NaOH} \longrightarrow \underset{154}{C_6H_4(NaO)_2} + 2Na_2SO_3 + 2H_2O$$

$$\begin{matrix} 362 & x & y \end{matrix}$$

$x = 205$ grams.

Therefore, in a fusion with 362 grams of sodium-benzene-di-sulfonate; theoretically, only 205 grams NaOH are required. But for best results, a great deal more caustic must be used for reasons stated previously.

y = 198 grams.

Therefore, the theoretical yield from 100 grams of benzene equals 198 grams of sodium resorcinate.

The amount of HCl necessary to acidify the fusion mass to neutrality is both a function of the amount of caustic used, and the manner in which the acid is added. By adding the acid so that it enters the fusion solution at the bottom, the SO_2 which is liberated is absorbed by the alkaline solution and thus helps materially to cut down the amount of acid actually used, and at the same time does away with the obnoxious SO_2 fumes.

The calculations for the amount of HCl required, assuming that the HCl does all the acidifying, and that $2\frac{1}{2}$ pounds of caustic were used for every pound of sodium salt, is as follows:

$$\underset{154}{C_6H_4(ONa)_2} + \underset{73}{2HCl} \rightarrow \underset{110}{C_6H_4(OH)_2} + 2NaCl$$

$$\begin{array}{cc} 198 & x \\ & y \end{array}$$

$x = 94$ $\qquad$ $y = 142.$

∴ The theoretical yield of resorcinol from 100 grams of benzene is 142 grams. The amount of HCl required to neutralize the sodium di-phenate equals 94 grams. 1 lb. of sodium salt for fusion requires $\frac{454}{362}$ x 205 = 256 grams caustic.

1135 - 256 = 879 grams caustic in excess.

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

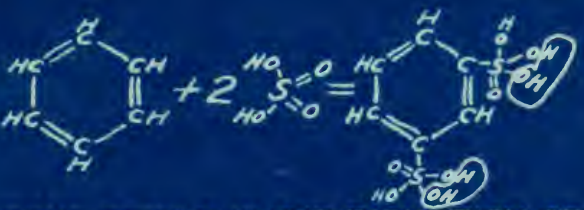
40 36.45

879 x x = 800 G.

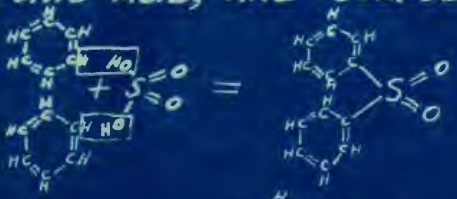
Therefore 800 grams HCl are required to acidify the excess NaOH. 1 pound of sodium salt after fusion theoretically gives 248 grams of sodium di-phenate: 248 grams of sodium di-phenate theoretically requires for neutralization $\frac{248}{198}$ x 94 = 118 grams of HCl. Therefore the total amount of HCl that is required to neutralize a fusion mass that was started with 2½ lbs. of caustic soda and 1 lb. of sodium salt; considering the sodium salt to be completely comverted, is 118+800 = 918 grams of HCl. The HCl acid to be used is Sp. G. 1.19 and 37% which therefore contains 1.19 x 0.37 = 0.44 gram HCl per cc. $\frac{918}{0.44}$ = 2090 cc of HCl of the above concentration which would be the amount theoretically required for complete neutralization.

REACTIONS INVOLVED IN THE PROCESS FOR MAKING RESORCINOL FROM BENZENE.

BENZENE + H_2SO_4

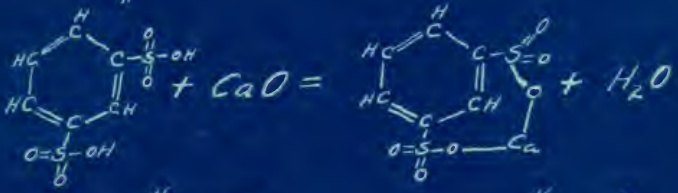


MINOR REACTIONS RESULT IN THE FORMATION OF ORTHO-AND PARA-DI-SULFONIC ACIDS, MONO-SULFONIC ACID, AND SULFOBENZID.

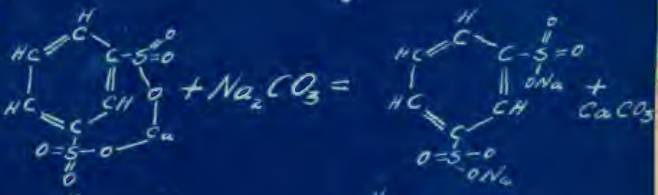


SULFOBENZID

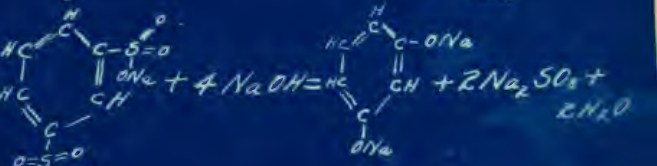
DISULFONIC ACID + LIME



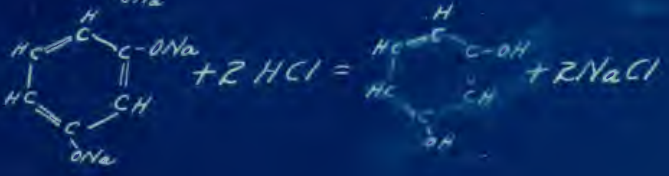
CALCIUM DISULFONATE + SODA ASH



SODIUM DISULFONATE FUSED WITH NaOH



SODIUM DI-PHENATE + HCl



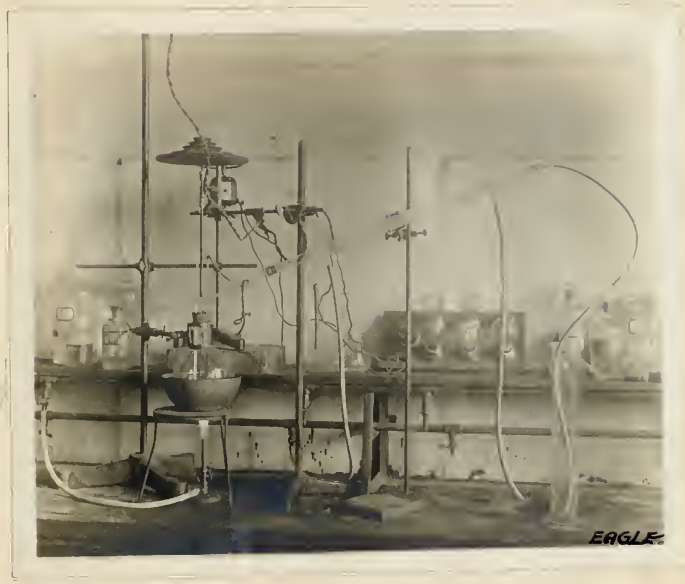
EXPERIMENTAL WORK.

First Experiment.

Sulfonation:

In sulfonating the benzene, we followed the procedure outlined under "Theoretical and Practical Considerations." As shown by the accompanying photograph, we used a round-bottomed, wide-mouth flask which was supported by a stand, and heated by an oil bath which was exposed to the direct flame of a blast burner. A glass stirring rod, the end of which was bent into a suitable form to provide for efficient stirring, passed through the middle hole of the rubber stopper which served as a bearing. The rubber stopper was covered with lead foil to prevent the corrosive action of the fuming sulfuric acid. A flexible joint was made by attaching a stout piece of rubber tubing to the end of the glass rod, about four inches above the rubber stopper, and using a steel rod as the upper shaft. The lower end of the steel rod projected into the rubber tubing and was made fast with a couple of twists of copper wire; the upper end of the steel rod was clamped to the revolving pulley which was connected to the motor pulley by means of a leather belt. Through one of the

Figure 2.



APPARATUS USED FOR SULFONATION.

other holes in the rubber stopper, a bent piece of glass tubing was inserted, and this was connected to the condenser as shown in the accompanying photograph. A 1cc pipette projected from another hole in the rubber stopper. By means of this pipeete and its attached piece of rubber tubing, samples of the contents of the flask were sucked up at stated intervals without stopping the stirring or in anyway hindering the smooth operation of the sulfonation. Through the last hole projected a thermometer, the bulb of which was immersed in the contents of the flask. By means of this thermometer, the temperature of the sulfonation mixture was determined at regular intervals. The two side stands were used as braces to keep the motor stand from vibrating. A bank of lamps was used as a rheostat to control the speed of the motor. The hose leading from the end of the condenser, passes into a measured amount of water in a graduate, and by this means all decomposed H_2SO_4 is absorbed.

In the first sulfonation, 200 grams of benzene, equivalent to $\frac{200}{0.879}$ or 228cc and 650 grams of 4% fuming acid, equivalent to $\frac{650}{1.87}$ or 348cc, were used. According to the calculations based upon theory, 500

grams of the 4% fuming acid are required. An excess of 150 grams, or 25% above the theoretical amount required, was therefore used.

The measured amount of H_2SO_4 was poured into the flask and everything was adjusted properly for an uninterrupted run. The oil bath was then heated until the contents of the flask were at about 60°C. The required amount of benzene was now poured slowly into the flask through the upper end of the condenser while the contents of the flask were undergoing continuous stirring. When all the benzene had been added, the flask contents were slowly brought up to the boiling point of benzene (80.36°) and kept around that temperature for three hours. At the end of the three hours, the temperature was raised with all possible speed to 255°, the highest temperature obtainable. The outside oil bath during this heating was maintained at 310°. The flask contents were kept at 255° for thirty minutes, and this completed the entire sulfonation. Continuous, even stirring was maintained by the motor, and samples were taken at 30 minute intervals; temperature readings were recorded every 15 minutes. A simple outline of the en-

tire run is shown by the accompanying data sheet labeled "Data Sheet for the First Sulfonation."

The samples taken at the proper intervals were drawn up by means of the pipette and poured into a weighed beaker which was instantly placed in a dessicator. An immediate weighing of the beaker and its contents was made, and by subtracting the original weight of the beaker, the amount of sample taken was determined. The free H_2SO_4 was then determined by adding an excess of $BaCl_2$ to a very dilute solution of the sample, boiling the solution containing the precipitated $BaSO_4$, filtering and drying the precipitate, igniting and then weighing. From the amount of $BaSO_4$ precipitated, the equivalent amount of free H_2SO_4 in the sample was determined, and from this the amount of free H_2SO_4 per gram of sample was calculated. The above quantitative determination is possible, due to the fact that the barium salt of the disulfonic acid is very soluble in water while the $BaSO_4$ is very insoluble.

Conversion to the Calcium Salt:

According to theory, the amount of lime required to neutralize the excess H_2SO_4 and the di-sulfonic acid,

Data Sheet for the First Sulfonation.

Time	Temperature	Remarks	Amount of Sample grams	Amount of $BaSO_4$ grams	Equivalent amount of 100% H_2SO_4 per gram of solution.
12:15	60°C	Start made	1.		
12:30	78°				
12:45	77°	Sample 1			
1:00	76°				
1:15	76°	Sample 2			
1:30	77°				
1:45	76°	Sample 3	NO DATA TAKEN		
2:00	75°				
2:15	77°	Sample 4			
2:30	75°				
2:45	75°	Sample 5			
3:00	77°				
3:15	76°	Sample 6			
3:30	250°	High temp. start. Slight temp. fluctuation			
3:45	255°	Sample 7			
4:00	255°	Finish.			

is 200 grams. But, due to the fact, that we were not working with pure CaO, and that the sulfonation did not go to completion, the amount actually required was 235 grams CaO.

The mass of benzene-di-sulfonic acid and excess H_2SO_4 from the sulfonation was first allowed to cool and was then poured into about five litres of water contained in an iron enamelled pan of about fifteen litres capacity. The solution thus formed was then brought up to boiling, and lime, which was thoroughly slaked, was then added slowly with continuous stirring until the solution showed an alkaline reaction towards litmus paper.

The boiling contents of the pan were then filtered hot with suction through an 8 inch Bückner funnel, and the residue of precipitated $CaSO_4$ and excess CaO was thoroughly washed with boiling water. The filtrate consisting of a slightly alkaline solution of calcium-benzene-di-sulfonate was now ready for conversion to the sodium salt.

Conversion to the Sodium Salt:

According to theory, the amount of Na_2CO_3 required for conversion of the calcium-benzene-di-sulfonate ob-

tained from 200 grams of benzene, is 272 grams. In the following operation, 300 grams of Na_2CO_3 were found necessary for complete conversion. This additional amount of Na_2CO_3 was probably the result of a slight excess of $Ca(OH)_2$ from the previous operation.

The solution of the calcium salt from the previous operation was boiled down to about five litres. A strong solution of Na_2CO_3 was then added to the boiling contents of the pan and at short intervals, a small amount of the contents was filtered and tested with Na_2CO_3. When a filtered sample showed no further precipitate of $CaCO_3$ upon the addition of Na_2CO_3, the conversion was complete, and no more Na_2CO_3 was added. Great care was taken that no excess of Na_2CO_3 was added, as this excess would be present in the salt used for fusion, and would be detrimental to best results for that operation.

The hot contents of the pan were now filtered as before through the Buckner funnel, and after thoroughly washing the precipitated $CaCO_3$, the very slightly alkaline solution of the sodium salt was brought down almost to dryness in the enamelled pan, and then

the salt was completely dried in a drying closet heated with steam coils. The dried salt was then pulverized to a very fine powder of about 200 mesh and it was now ready for fusion.

According to theory, the amount of sodium salt that should be obtained, is 724 grams. We only obtained 650 grams. The difference can be accounted for by the fact that we did not have a complete sulfonation to the di-sulfonic acid, and to a lesser extent by the fact that the precipitates were not thoroughly washed to free them of all soluble salts. The "silver salt" was a creamy white in color.

Fusion.

In the fusion of the sodium salt derived from the first sulfonation, one pound of the dry salt was used with one pound of alkali: The caustic that was used analyzed 86% NaOH, 2% NaCl, 7% Na_2SO_4, 3% Na_2CO_3, and 2% H_2O. To get one pound of caustic NaOH as such, $\frac{1.00}{0.86}$ or 1.163 pounds of the commercial product was used. According to theory, 4 molecules of NaOH are required for each molecule of sodium salt. Therefore 0.57# of NaOH are required for each pound of dry salt assuming it to be 100% sodium-benzene-di-sulfonate.

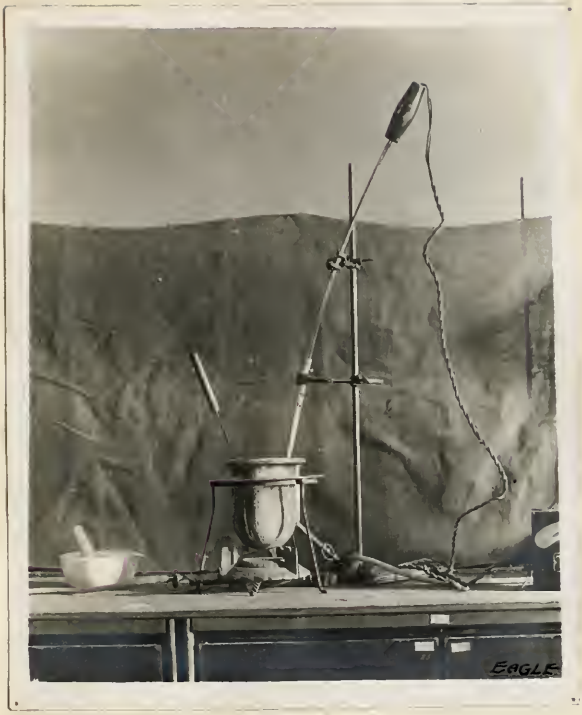
$$\frac{4NaOH}{C_6H_4(SO_3Na)_2} = \frac{x}{1} \qquad x = \frac{1x160}{282} = .57^{\#}$$

Therefore, in using $1^{\#}$ of sodium salt in the fusion, there is an excess of $.43^{\#}$ equal to 75.5% of the amount actually required.

In this fusion and all subsequent fusions, the apparatus consisted of the fusion pot supported on a Rose burner, with an extra blast burner as an auxiliary source of heat. A Hoskins pyrometer whose fire end consisted of nickel-chrome alloy, was used for temperature control. As no mechanical means for stirring the fusion mass was available, the large iron spatula shown in the photograph was used for this operation.

The NaOH was placed in the fusion kettle and brought up to the desired temperature, in this fusion between 340°-345°, at which temperature the contents of the kettle were liquid. Maintaining the temperature very closely between 340° and 345°, the sodium salt was gradually added, allowing one part of the salt to be thoroughly assimilated before the next part was added. Throughout the above operation, the stirring was kept continuous and uniform. One half hour was required to assimilate the pound of salt used.

Figure 3.



APPARATUS USED FOR FUSION.

After all the salt had been added, the fusion mass was closely kept at 340° with continuous stirring for 1 ¾ hours. At the end of this time the fusion was considered to be complete. The fusion mass was very viscous and dark brown in color. It was now poured into a pail containing five litres of water and kept there until it was thoroughly dissolved.

Neutralization of the Fusion Mass:

Theory requires 710cc of HCl (Sp. G. 1.19 Conc. 37%) to neutralize the entire fusion mass obtained from 1# NaOH and 1# sodium salt, upon the assumption that the sodium salt is 100% sodium-benzene-di-sulfonate and that the fusion products are exactly those that theory shows. In the following acidification, 1000 cc of the HCl were used, the excess being required for the impurities that were present with the caustic.

A measured amount of acid in a separatory funnel was allowed to flow slowly into the solution of the fusion mass contained in an enamelled pail. The acid was allowed to enter the solution near the bottom, and was added with continuous stirring until the first trace of SO_2 was detected. The solution was now

acid towards litmus paper and was evaporated down to about $1\frac{1}{2}$ litres and allowed to cool. The tar and precipitated salts, consisting mainly of NaCl, were then filtered off by means of a Buckner funnel, and thoroughly washed. In the boiling of the solution, the SO_2 had been driven off, and the above filtrate now reacted alkaline towards litmus. It was acidified further by the addition of a small amount of HCl and boiled down again to about $\frac{3}{4}$ litres and allowed to cool, when a further precipitation of salts occurred. These salts were thoroughly washed and the resulting filtrate from the second boiling was again subjected to the same treatment for the third time. In this way, the major part of the salts was removed, while the resorcinol was still retained in solution due to its very great solubility in water (117 grams of resorcinol being soluble in 100 grams of water at 25°) The solution, after the third filtration, was then brought down to dryness in the drying closet, and the resulting mass of dry dark-colored salts was pulverized by means of a mortar and pestle. These salts containing the resorcinol, were now ready for extraction with alcohol.

Table of Solubilites.

Temp.	In H_2O Sp.G. of Sol.	In H_2O Grams $C_6H_4(OH)_2$ per 100g. H_2O	In H_2O Grams $C_6H_4(OH)_2$ per 100g. Sol	In Ethyl Alcohol Sp.G. of Sol.	In Ethyl Alcohol Grams $C_6H_4(OH)_2$ per 100g Alcohol	In Ethyl Alcohol Grams $C_6H_4(OH)_2$ per 100g Sol
0	1.101	60	37.5	1.033	210	
10	1.118	81	44.8	1.036	223	
20	1.134	103	50.7	1.04	236	
25	1.142	117	53.9	1.045	243	
30	1.148	131	56.7	1.048	250	
40	1.157	161	58.9	1.056	266	
50	1.165	198	66.5	1.065	286	
60	1.172	246	71.1	1.075	311	
70	1.176	320	76.2	1.087	341	
80	1.179	487	82.9	1.104	375	

Speyers Am. J. Sci. (4) 14,294,'02.

Solubility of Resorcinol in Alcohols and Acids.

Timofeiew, 1894.

Solvent	t°	Grams $C_6H_4(OH)_2$ per 100g. sat. sol.
Methyl alcohol.	11.6°	69
Propyl "	10.4	51.5
Propyl "	11.6	51.6
Formic acid	15	29.2
Acetic "	15	32.5
Propionic "	15	22.8
Butyric "	15	14.7

Extraction of Resorcinol from the Dry Salts by means of Alcohol:

Resorcinol is very soluble in water, ethyl alcohol, methyl alcohol, propyl alcohol, and to a lesser extent in formic acid, acetic acid, propionic acid, and benzene. The solubility of resorcinol in these various solvents is shown on another page. Considering the cost of the solvent, its adaptability to the extraction of the resorcinol from the dry salts, and the efficiency of the subsequent recovery of the solvent after its use in extraction, alcohol, by far, leads the other solvents. Alcohol was therefore chosen as the solvent to be used in our experiments. Pure 95% ethyl alcohol was used in our work, but the same results are obtainable with denatured alcohol which can be secured at a much cheaper rate (Denatured alcohol at the present market is 77¢ a gallon.)

In the extraction with alcohol, the 400 grams of dry salts obtained from the previous operation were placed in a wide-mouth 2 liter flask and thoroughly shaken up with 300cc alcohol. The resulting alcoholic solution of resorcinol was filtered off

from the salts which did not dissolve, through a Buckner funnel. The above operation was repeated with portions of 100cc of alcohol until the filtrate came through colorless. To accomplish this, 1300cc of alcohol were required. The filtrate was a dark red color due to the presence of tarry bodies which are also dissolved by the alcohol. The alcoholic filtrate only amounted to 1200cc; the difference between the amount of alcohol used and the amount recovered, 100cc, is due to the fact that the salts after the filtration were wet with alcohol. Commercially, the recovery of the alcohol could be made almost 100% complete by heating the extracted salts in a suitable chamber and condensing the alcohol vapors.

Liberation of the Resorcinol:

The 1200 cc of the alcoholic resorcinol solution obtained from the previous operation were distilled down to about 100cc in a distilling flask with a suitable condenser and receiver. The 100cc residue, of a very dark red color, which showed the presence of considerable tar, was allowed to cool and a small amount of salt precipitated out. This salt

had dissolved in the 5% H_2O which was present in the alcohol. The solution was then carefully poured off from the salt into a 150cc Fry glass distillingflask.

The distilling flask was connected to a small bottle receiver by means of glass tubing and rubber tubing, and this receiver was in turn connected to the vacuum pump. A thermometer was inserted through the cork stopper in the neck of the distilling flask and the bulb extended down below the outlet tube. All connections and stoppers were made airtight with beeswax. In the subsequent vacuum distillation, it was found that the resorcinol came over at 150°C as a water white liquid which solidified at the first connection where rubber tubing was used due to its high melting point (116°C) Further distillation was therefore stopped and a new set up of the apparatus had to be evolved. The solution of the problem was finally obtained by setting up the apparatus as shown in the accompanying photograph.

The distilling flask supported in a sand bath and heated by a blast burner, was connected by a very short piece of tough, thin, rubber tubing to a safety bulb which was directly connected to the motor driven,

Cenco, double-stage, oil vacuum pump. A low flame from a Bunsen burner was utilized to keep the stem from the neck of the distilling flask to the entrance in the safety bulb, at a temperature above 116°. The resorcinol vapors were therefore kept from condensing in the stem, but they were caught and condensed in the safety bulb. This did not stop the distillation as the solidification occured in the bottom of the bulb and allowed a free passage for the vacuum pump to operate in. The reason a retort was not used instead of a distilling flask was due to the fact that the retort could not be made airtight. The wax which was used to make the cork stopper airtight melted and flowed down the side on account of the heat of the sand bath.

The resorcinol, under a vacuum of about 1 cm. came over at 150°C. The first distillate was water white, but as the distillation went on, the resorcinol became contaminated with some tar and at the last stage of the distillation, the color was red. The amount obtained from this first experiment was 23 grams of impure resorcinol whose melting point was 95°C. The resorcinol, at the above melting point, would correspond to about 90% purity.

Figure 4.

APPARATUS USED FOR VACUUM DISTILLATION.

Second Experiment.

In the second sulfonation, the same procedure was followed as in the first, except that in sulfonating 200 grams of benzene which is equivalent to $\frac{200}{.879}$ or 228cc, there were used 700 grams of 4% fuming acid which is equivalent to $\frac{700}{1.869}$ or 375cc, instead of 650 grams of the acid. The time of sulfonation was $3\frac{3}{4}$ hours and samples were taken at regular intervals as before. The data sheet for this run is shown on the next page, and the progress and rate of sulfonation is shown by the accompanying graph.

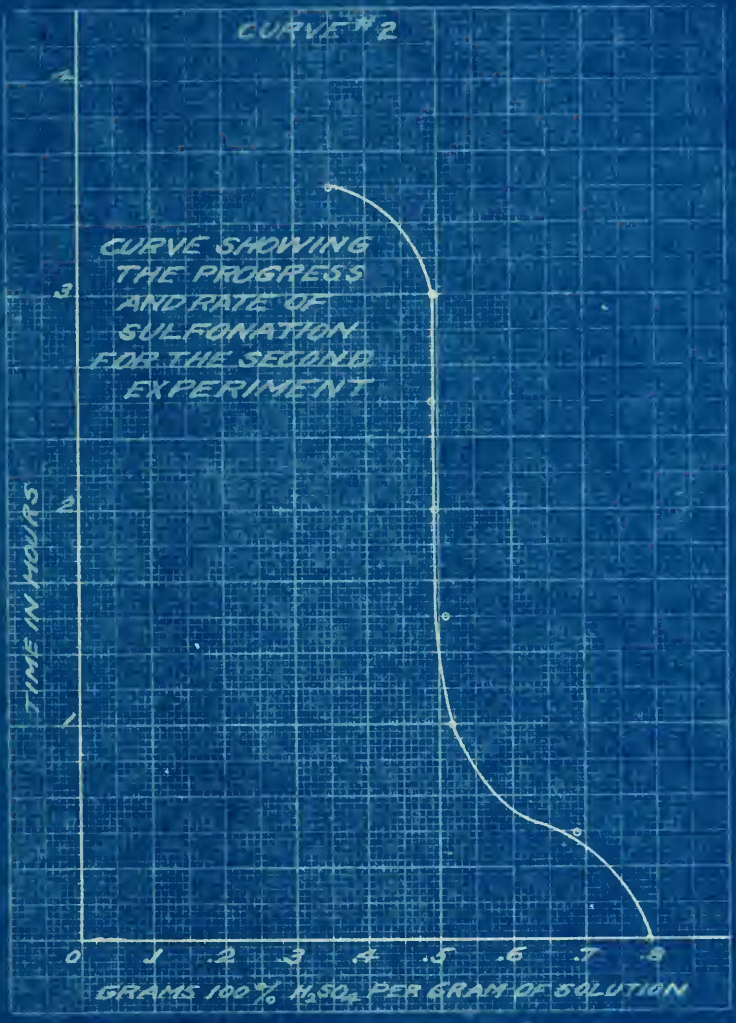
The conversion to the calcium salt and the elimination of the excess H_2SO_4 was accomplished as in the first experiment. Here, 260 grams of CaO were required due to the greater amount of acid used.

The conversion to the sodium salt was made as in the first experiment, with the same precautions and amount of Na_2CO_3. The amount of dry sodium-benzene-di-sulfonate obtained was equal to 640 grams. This "silver salt" had a slight pinkish hue.

In the fusion of the sodium salt derived from the second experiment, $1\frac{1}{2}^{\#}$ caustic NaOH was used with $1^{\#}$ of salt. The temperature was closely con-

Data Sheet for the Second Sulfonation.

Time	Temp.	Remarks	Amount of sample grams	Amount of $BaSO_4$ grams	Equivalent amount of 100% H_2SO_4 per gram of solution.
12:00	60°	Start made			.79
12:15	81°				
12:30	80°	Sample 1.	1.2075	1.9895	.693
12:45	75°				
1:00	80°	Sample 2.	1.6755	2.0735	.52
1:15	78°				
1:30	77°	Sample 3.	1.5100	1.8320	.51
1:45	76°				
2:00	78°	Sample 4.	1.3775	1.6240	.496
2:15	78°				
2:30	77°	Sample 5.	1.4328	1.6875	.494
2:45	78°				
3:00	80°	Sample 6.	1.5823	1.8582	.493
3:15	220°	High temp. start.			
3:30	265°	Slight temp. fluctuation.			
3:45	260°	Sample 7.	1.2595	1.0550	.352


CURVE # 2
CURVE SHOWING THE PROGRESS AND RATE OF SULFONATION FOR THE SECOND EXPERIMENT
TIME IN HOURS
0
1
2
3
4
.1
.2
.3
.4
.5
.6
.7
.8
GRAMS 100% H_2SO_4 PER GRAM OF SOLUTION

trolled between 320° and 325° and the time of the fusion was 2 hours. The resulting fusion mass was a yellowish-brown color very much less viscous than the first fusion mass. It hardened quickly upon cooling, the hardened mass being difficultly soluble in H_2O. The entire contents of the fusion kettle were dissolved in water.

In the neutralization of the fusion mass solution, 1750cc of HCl were required. The acid was added, as explained before, by means of a separatory funnel. The major part of the salts were eliminated as before, the remaining salts being brought down to dryness. This gave 450 grams of the dry salt which was black and tarry looking. These salts were then pulverized.

In the extraction of the resorcinol from the dry salts, 1570cc of alcohol were used before the filtrate from the final portion came through colorless. The first portion was of 300cc and the succeeding portions of 100cc. The filtrate recovered was 1450cc and was of a deep red color due to the presence of tar.

The resorcinol obtained from the alcoholic solution was obtained as outlined before. Due to the

presence of a small amount of phenol and tar, the resorcinol was of an orange-red color. This resorcinol was not purified any farther. Its melting point was 98°C. The yield was 39.8 grams.

Third Experiment.

In the third sulfonation, 720 grams of 4% fuming acid were used with 200 grams of benzene. The same procedure as before was followed, but the time of sulfonation here was 4 hours and eleven samples were taken at regular intervals. The data sheet for this run is shown on the next page, and the progress and rate of sulfonation is illustrated by the accompanying graph.

In the conversion to the calcium salt and the elimination of the excess H_2SO_4, 300 grams of CaO were required.

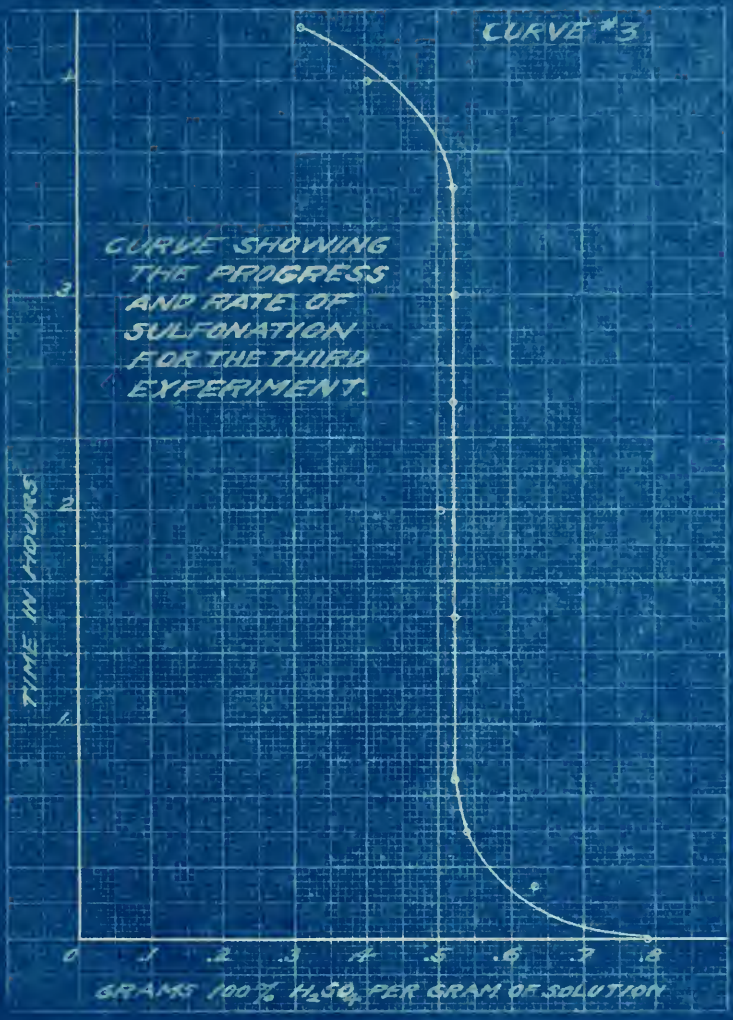
The conversion to the sodium salt was accomplished as before with the same amount of Na_2CO_3 and 635 grams of the dry sodium salt were obtained. This salt, of a slight pink color, was pulverized very finely.

In the fusion, $1\frac{1}{2}$# NaOH and 1# of sodium salt were used exactly as in the second experiment, except that the temperature was closely controlled between 340° and 345° for 2 hours. The fusion mass was a very dark brown and slightly more viscous than the second fusion mass. This was poured into about 4 litres of water and solution took place rather readily.

Data Sheet for the Third Sulfonation.

Time	Temp.	Remarks	Amount of Sample grams	Amount of $BaSO_4$ grams	Equivalent amount of 100% H_2SO_4 per gram of solution.
2:20	60°	Start			
2:35	82°	Sample 1	1.2355	1.8710	.635
2:50	80°	Sample 2	1.3936	1.7848	.538
3:05	80°	Sample 3	1.3515	1.6900	.526
3:20	78°	Sample 4	Spilled		
3:35	76°				
3:50	75°	Sample 5	1.2940	1.6212	.526
4:05	76°				
4:20	78°	Sample 6	1.4688	1.7536	.503
4:35	80°				
4:40	80°	Sample 7	1.5918	1.9885	.524
5:05	80°	Sample 8	1.3400	1.6886	.528
5:10	95°				
5:15	160°				
5:20	200°	Sample 9	1.2749	1.5835	.522
5:25	235°	Temp.			
5:30	251°	fluctuates			
5:37	236°	Sample 10	1.3116	1.2687	.406
5:45	270°				
5:50	270°				
5:55	260°				
6:15	270°				
6:25	230°	Sample 11 Finish	1.0248	0.7550	0.31

Data


CURVE #3
CURVE SHOWING THE PROGRESS AND RATE OF SULFONATION FOR THE THIRD EXPERIMENT.
TIME IN HOURS
1
2
3
4
0
.1
.2
.3
.4
.5
.6
.7
.8
GRAMS 100% H_2SO_4 PER GRAM OF SOLUTION

In the neutralization, 1670cc HCl were used. Most of the salts were eliminated as before, and 500 grams of dry salts were obtained, which were pulverized. These salts were black and tarry looking. In bringing the salts down to dryness in an electrically heated drying closet, a high temperature was accidentally maintained for about 2 hours. Sublimed crystals of resorcinol were discovered upon the door of the closet which fact accounts for the subsequent poor yield of resorcinol.

1300cc of alcohol were used in the extraction of the resorcinol and the filtrate consisting of 1230cc was of a dark red color.

The resorcinol obtained by a vacuum distillation was of a deep red color due to the presence of considerable impurities. Its melting point was 90°C and the yield was 12 grams.

Fourth Experiment.

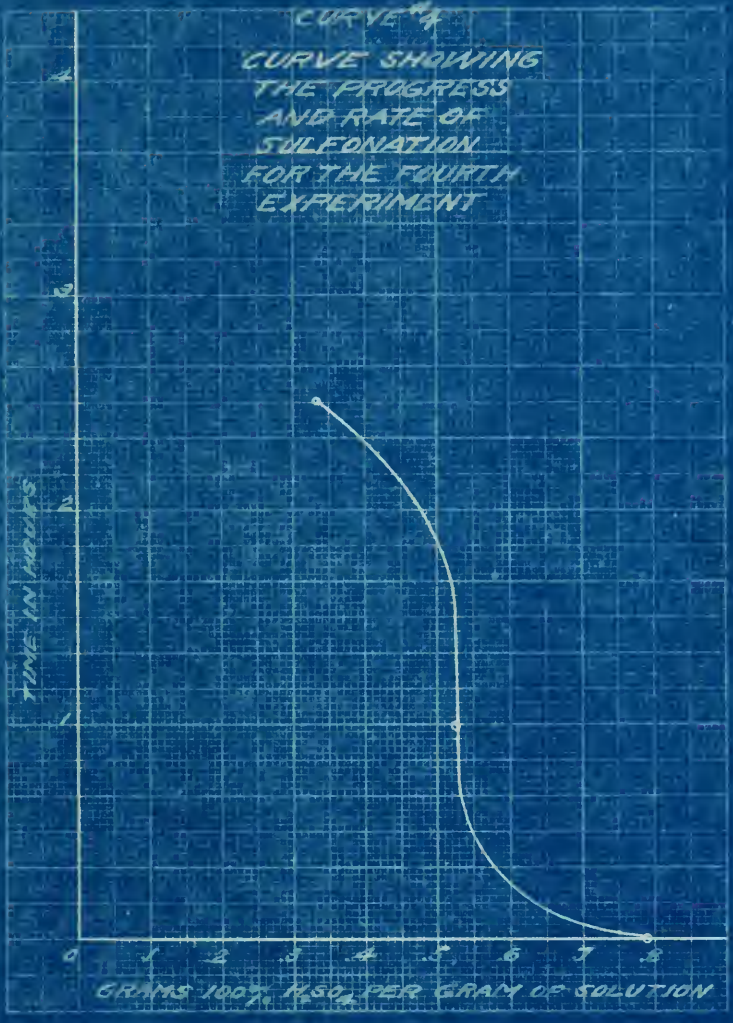
In the fourth sulfonation, 740 grams of 4% fuming acid were used with 200 grams of benzene. Since the graphs for the second and third sulfonation show that no progress is made and that nothing is accomplished by heating the sulfonation mixture for more than 1 hour at 80°, it was determined to cut the time for the sulfonation down to $2\frac{1}{2}$ hours for this complete sulfonation by eliminating $1\frac{1}{2}$ hours of heating at 80°. The time of sulfonation was therefore $2\frac{1}{2}$ hours and 3 samples were taken. The data for this run is shown on the next page, and the progress and rate of sulfonation are illustrated by the accompanying graph.

The conversion to the calcium salt and the subsequent conversion to the sodium salt were followed out as before, with practically the same amounts of reagents. The dried sodium salt, of a creamy white color, was finely pulverized and the yield was 650 grams.

In the fusion $1\frac{1}{2}$# NaOH were used with 1# of the "silver salt", and the temperature was maintained closely between 340° and 345° for $2\frac{1}{4}$ hours. The fusion

Data Sheet for the Fourth Sulfonation.

Time	Temp.	Remarks	Amount of sample grams	Amount of $BaSO_4$ grams	Equivalent amount of 100% H_2SO_4 per gram of solution
10:48	60°	Start made			
11:03	82°				
11:18	78°				
11:33	77°				
11:48	80°	Sample 1	1.1471	1.4365	.526
12:03	150°				
12:18	267°				
12:33	265°	Slight temp. fluct-ations			
12:48	252°				
1:03	260°				
1:18	250°	Sample 2	1.3099	1.0435	.335


CURVE #4
CURVE SHOWING THE PROGRESS AND RATE OF SULFONATION FOR THE FOURTH EXPERIMENT
TIME IN HOURS
0
1
2
3
4
5
6
7
8
GRAMS 100% H_2SO_4 PER GRAM OF SOLUTION

mass was a dark brown and viscous. This was dissolved in about 4 litres of water.

In the neutralization, 1650cc HCl were used. The salts were eliminated as before, and 500 grams of dry salts were obtained which were pulverized very finely. These salts were black and tarry looking.

1450cc alcohol were used for the extraction and the recovered alcohol was only 1350cc. The filtrate was a deep red color showing the presence of considerable tar.

The resorcinol obtained by a vacuum distillation was of a deep red color showing the presence of considerable impurities. The yield was only 18 grams.

Fifth Experiment.

In the fifth sulfonation, the same amounts of benzene and acid were used as in the fourth experiment. The time of sulfonation was cut down to $2\frac{1}{4}$ hours. The data for this run is shown on the next page, and the progress and rate of sulfonation are illustrated by the accompanying graph.

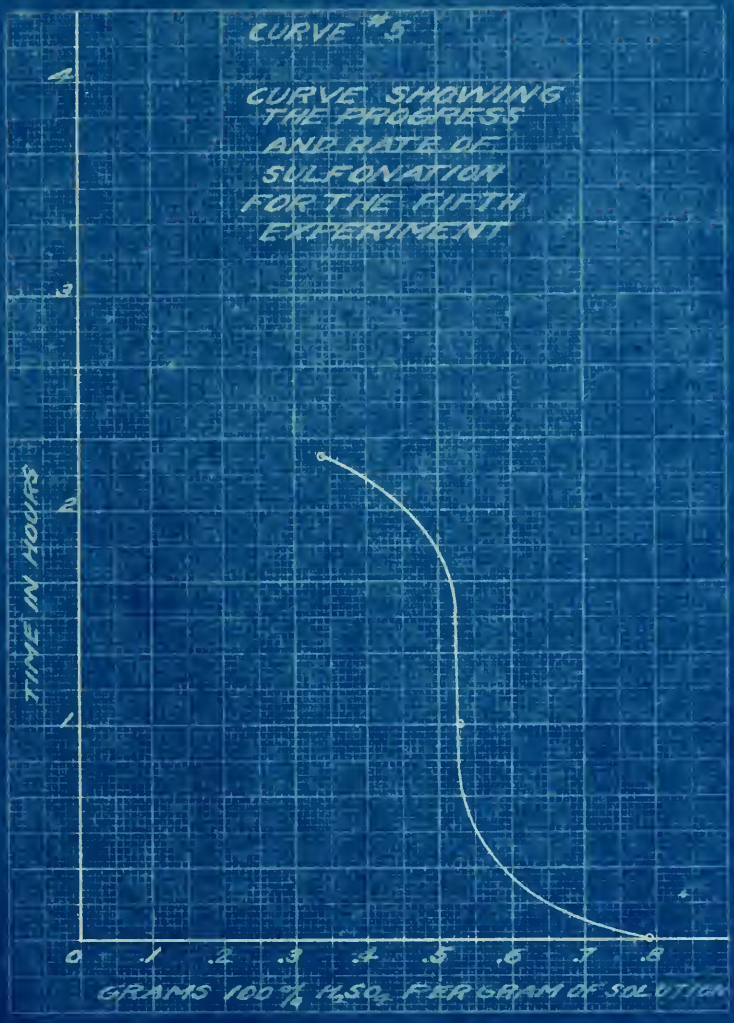
The conversion to the calcium salt and after this, the conversion to the sodium salt was accomplished as outlined before. The dried sodium salt of a creamy white color was finely pulverized with a mortar and pestle. The yield of the sodium salt was 670 grams.

In the following fusion, a radical change was made. It was determined to follow commercial practice, and in this fusion, $2\frac{1}{2}^{\#}$ of NaOH were used with $1^{\#}$ of "silver Salt" and the temperature was closely maintained between 280° and 285° for $6\frac{1}{2}$ hours. The resulting fusion mass was light brown and viscous and it was dissolved in about five litres of water.

In the neutralization, due to the greater excess of NaOH, 2600cc HCl were used. The major part of the salts were eliminated as before and 625 grams

Data Sheet for the Fifth Sulfonation.

Time	Temp.	Remarks	Amount of Sample grams	Amount of $BaSO_4$ grams	Equivalent amount of 100% H_2SO_4 per gram of solution
2:30	60^0	start made			
2:45	83^0				
3:00	79^0				
3:15	95^0				
3:30	78^0	Sample 1	1.2928	1.6300	.53
3:45	230^0				
4:00	258^0				
4:15	260^0				
4:30	266^0				
4:45	230^0	Sample 2	1.6050	1.2945	.339


CURVE #5
CURVE SHOWING THE PROGRESS AND RATE OF SULFONATION FOR THE FIFTH EXPERIMENT
TIME IN HOURS
4
3
2
1
0
.1
.2
.3
.4
.5
.6
.7
.8
GRAMS 100% H_2SO_4 PER GRAM OF SOLUTION

of the dry salts were finally obtained. These salts were much different from the preceding salts in color, which in this case was a light gray. During the drying of these salts, the presence of a large amount of resorcinol was shown by the sublimation of long needles of resorcinol upon the surface of the dry salts.

In the extraction, 1450cc of alcohol were used and 1370cc of alcohol were recovered. The alcoholic extract of resorcinol was a light orange color, which fact denoted the absence of considerable tar.

The vacuum distillation was made in two parts. The water white resorcinol distillate which came over at 150°C during the first part of the distillate, after a short time began to come out colored a slight red. The distillation was stopped at this point and the pure resorcinol was extracted from the bulb with alcohol and then the second distillation was continued until no further distillate was obtained. The final distillate came out red. There were 22 grams of pure resorcinol whose melting point was 109° which corresponded to a purity of about 98.5% and there were 42

grams of the impure resorcinol whose melting point was 98°. The total yield was 64 grams, which was the largest yield obtained and this yield bore out the conclusion made from the color of the alcoholic filtrate from the dry salts.

Sixth Experiment

In the sixth sulfonation, the same amounts of benzene and acid were used as in the fourth experiment. The time of sulfonation was cut down to 2 hours. The data for this run is shown on the next page, and the progress and rate of sulfonation are illustrated by the accompanying graph.

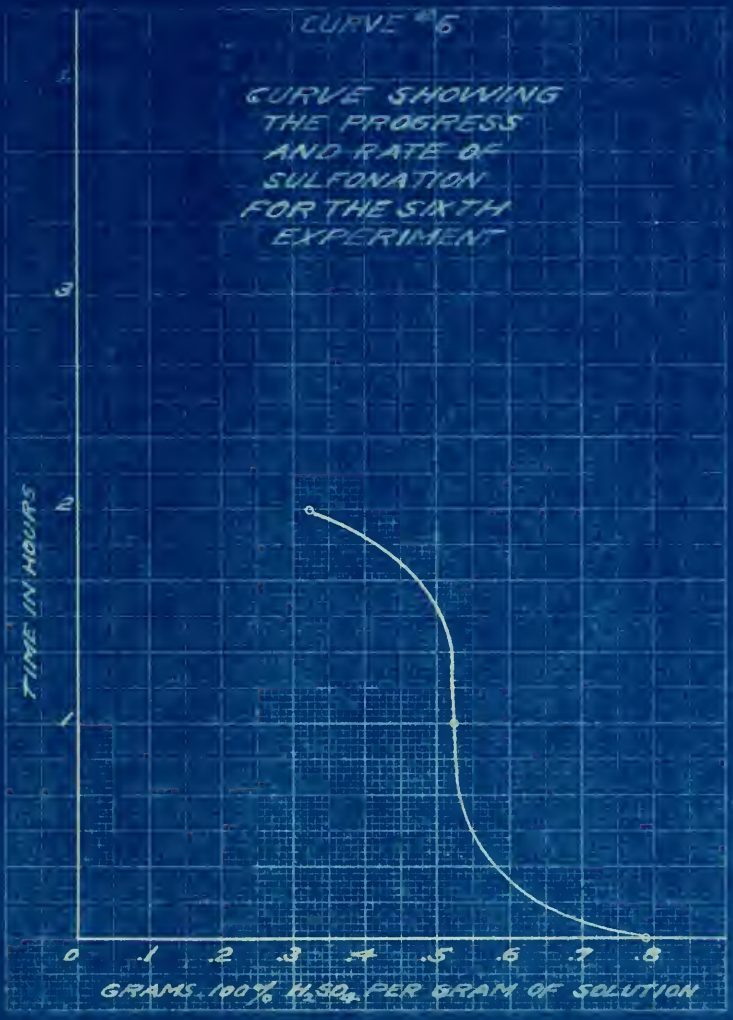
The conversion to the calcium salt and the subsequent conversion to the sodium salt were accomplished as before. The dried sodium salt, of a creamy white color, was finely pulverized and the yield was 685 grams.

In the fusion, $2\frac{1}{2}^{\#}$ NaOH were used with $1^{\#}$ of sodium salt. The temperature was maintained very closely between 290° and 295° for $7\frac{1}{4}$ hours. The dark brown and viscous fusion mass was dissolved in water.

2550cc HCl were used in the neutralization and the major part of the salt was eliminated in the usual way. Upon making a qualitative test of the salt residue, no trace of resorcinol was found. We therefore concluded there was no resorcinol in the

Data Sheet for the Sixth Sulfonation.

Time	Temp.	Remarks	Amount of sample grams	Amount of $BaSO_4$ grams	Equivalent amount of 100% H_2SO_4 per gram of solution
2:10	60°	start made			
2:25	80°				
2:40	82°				
2:55	81°				
3:10	80°	Sample 1	1.3900	1.739	.525
3:25	80°				
3:40	130°				
3:55	265°				
4:10	220°	Sample 2	1.2465	.9640	.325


CURVE #6
CURVE SHOWING THE PROGRESS AND RATE OF SULFONATION FOR THE SIXTH EXPERIMENT
TIME IN HOURS
3
2
1
0
.1
.2
.3
.4
.5
.6
.7
.8
GRAMS 100% H_2SO_4 PER GRAM OF SOLUTION

salts as in all our previous experiments, we got a test for resorcinol in the dry salts. We therefore, decided that further experimentation was useless, and since our time was limited, we decided to stop further work.

To prove that the decomposition of the H_2SO_4 in sulfonating at the high temperature was negligible, all the distillate coming over was caught in the graduate containing 500cc H_2O.. The final amount of solution in the graduate was 114cc, showing that 64cc of solution was distilled over. Of this amount, about 1cc was benzene which was $\frac{1}{2}\%$ of the amount originally used.

To test for SO_2 present in the distillate, a 2cc sample was titrated with an iodine solution of which 1cc $\equiv$ .01238gI_2. 13.3ccI_2 solution were required $\equiv$ 13.3x.01238 $\equiv$ .1646gI_2.

$$\underset{64}{SO_2} + \underset{2\times 54}{2H_2O} + I_2 \longrightarrow \underset{98}{H_2SO_4} + 2HI$$

$$\begin{matrix} x & .1646 & y \end{matrix}$$

$x = .0415$

$\therefore$ 2cc of solution $\equiv$ .0415g. SO_2.

$\frac{114}{2} \times .0415 = 2.3655$g. SO_2.

$y = .0635$g $H_2SO_4 \equiv .0415$g SO_2

2.3655g $SO_2 \equiv 3.62$g H_2SO_4

After titrating the above sample the total H_2SO_4 present was determined with $BaCl_2$ and the weight of $BaSO_4$ was found to be 0.1683 grams. Equivalent amount H_2SO_4 is .1683 x .4201 = .0707g. H_2SO_4. H_2SO_4 due to oxidation of SO_2 = .0635g/2cc H_2SO_4 present as SO_3 which was driven over = .0707-.0635 = .0072g per 2cc.

$\frac{114}{2}$ x .0072 = .4104 g. H_2SO_4 ≡ .335g SO_3.

On the basis of the amount of acid used to start with, the amount decomposed in the process of sulfonation is plainly negligible.

Discussion of Graphs.

Sulfonation:

In the second experiment, 700 grams of 4% fuming acid were used with 200 grams of benzene in the sulfonation. The total amount of solution was therefore equal to 900 grams in which there are 7 x 100.9 or 706.3 grams of 100% H_2SO_4.

$\frac{706.3}{900} = .785$

∴ 1 gram of solution at the beginning of the sulfonation contains 0.785 grams of 100% H_2SO_4 and this gives the first point on the curve for the second sulfonation. In the same manner, the first points for the other curves were obtained.

If no material is lost during the sulfonation operation, then the contents of the flask would still be 900 grams after the complete sulfonation. According to theory, 200 grams of 100% H_2SO_4 should be left after complete sulfonation to the disulfonic acid, if the start was made with 700 grams.

$\frac{200}{900} = .223$

T

FUSION MASS	NEUTRALIZATION		EXTRACTION			RESORCINOL					
	AMOUNT OF HCl USED (SP. G. 1.19 CONC 37%) - CC.	AMOUNT DRY SALT OBTAINED - GRAMS.	AMOUNT ALCOHOL USED - CC.	APPEARANCE OF ALCOHOLIC EXTRACT.	AMOUNT OF ALCOHOL RECOVERED - CC.	AMOUNT OBTAINED GRAMS	APPEARANCE	MELTING POINT °C.	PERCENT YIELD ON BASIS OF C_6H_6 USED	PER CENT YIELD ON BASIS OF 100% SODIUM SALT.	PER CENT YIELD ON BASIS OF ACTUAL AMOUNT OF SODIUM-BENZENE-DI-SULFONATE PRESENT AS SALT.
DARK BROWN	1000	400	1300	DARK RED	1200	23	RED	95°	8.05%	12.8%	17.5%
BROWN FLOW	1750	450	1570	DARK RED	1450	39.8	RED	98°	14%	22.4%	40.8%
VERY DARK BROWN	1670	500	1300	DARK RED	1230	12	DARK RED	90°	4.2%	6.7%	9.15%
DARK BROWN	1650	500	1450	DARK RED	1350	18	DARK RED	—	6.4%	10.1%	14.2%
LIGHT BROWN	2600	625	1450	LIGHT ORANGE	1370	64	1st PORTION IS WHITE 2nd PORTION IS SLIGHT RED	109° 98°	22.2%	36%	53.8%
DARK BROWN	2550	—	—	—	—	—	—	—	—	—	—

SUMMARY SHEET

	SULFONATION									CONVERSION				FUSION								NEUTRALIZATION	EXTRACTION				RESORCINOL				
	AMOUNT 4% FUMING H_2SO_4 GRAMS	AMOUNT OF BENZENE GRAMS	EXCESS H_2SO_4 GRAMS	PERCENT EXCESS H_2SO_4	HIGHEST TEMPERATURE OBTAINED	CONCENTRATION AFTER CONCETE SULFONATION GRAMS 100% H_2SO_4 PER GRAM OF SOLUTION	TIME FOR COMPLETE SULFONATION - HOURS	TIME TO COMPLETE MONO-SULFONATION HOURS	AMOUNT OF SULFONATION TO DI-SULFONIC ACID ACCORDING TO CURVE	AMOUNT LIME USED - GRAMS	AMOUNT SODIUM CARBONATE USED GRAMS	AMOUNT SODIUM SALT OBTAINED GRAMS	AMOUNT OF SODIUM SALT ACCORDING TO THEORY - GRAMS	AMOUNT NaOH USED POUNDS	EXCESS NaOH POUNDS	PERCENT EXCESS NaOH	AMOUNT SODIUM SALT USED FOR FUSION - POUNDS	AMOUNT SODIUM SALT PRESENT AS SULFONIC CORRECTED TO CURVES	TEMPERATURE OF FUSION °C.	TIME OF FUSION HOURS	APPEARANCE OF FUSION MASS	AMOUNT OF HCl USED (SP. G. 1.19 CONC 37%) - CC.	AMOUNT DRY SALT OBTAINED - GRAMS.	AMOUNT ALCOHOL USED - CC.	APPEARANCE OF ALCOHOLIC EXTRACT	AMOUNT OF ALCOHOL RECOVERED CC.	AMOUNT OBTAINED GRAMS	APPEARANCE	MELTING POINT °C.	PERCENT YIELD ON BASIS OF 6% USED	PER CENT YIELD ON BASIS OF 100% SODIUM SALT	PER CENT YIELD ON BASIS OF SODIUM SALT PRESENT AS DI-SULFONIC ACID
Exp. I	650	200	150	30%	255°	—	3½	—	—	235	300	650	724	1.0	.43	75%	1	—	340	1¾	DARK BROWN	1000	400	1300	DARK RED	1200	23	RED	95°	8.05%	12.8%	17.5%
Exp. II	700	200	200	40%	265°	.35	3½	1	55%	260	300	640	724	1½	.93	163%	1	.55#	320	2	BROWN YELLOW	1750	450	1570	DARK RED	1450	33.8	RED	98°	14%	22.4%	40.8%
Exp. III	720	200	220	44%	270°	.31	4	1	74%	300	300	635	724	1½	.93	163%	1	.74#	340	2	VERY DARK BROWN	1670	500	1300	DARK RED	1230	12	DARK RED	90°	4.2%	6.7%	9.15%
Exp. IV	740	200	240	48%	267°	.33	2½	1	71%	340	310	650	724	1½	.93	163%	1	.71#	340	2¼	DARK BROWN	1650	500	1460	DARK RED	1350	18	DARK RED	—	6.4%	10.1%	14.2%
Exp. V	740	200	240	48%	266°	.34	2¼	1	67%	340	310	670	724	2½	1.93	340%	1	.67#	280	6½	LIGHT BROWN	2600	625	1450	LIGHT ORANGE	1370	64	IN ALC. SOLN. IS WHITE - IN H₂O SOLN IS LIGHT RED	109° - 98°	22.2%	36%	55.8%
Exp VI	740	200	240	48%	265°	.325	2	1	73%	340	310	685	724	2½	1.93	340%	1	.73#	290	7¼	DARK BROWN	2550	—	—	—	—	—	—	—	—	—	—

∴ the final concentration of H_2SO_4 left in the contents of the flask if the sulfonation to the di-sulfonic acid is complete should be 0.223 grams 100% H_2SO_4 per gram of solution.

To complete the mono-sulfonation for 200 grams of benzene, 251.7 grams 100% H_2SO_4 are required. The start was made with 706.3 grams 100% H_2SO_4. 706.3 - 251.7 = 454.6 grams 100% H_2SO_4 which should be left after the sulfonation to the mono-sulfonic acid is complete.

$\frac{454.6}{900}$ = 0.505 grams.

∴ the final concentration of H_2SO_4 after the mono-sulfonation is complete should be 0.505 grams 100% H_2SO_4 per gram of solution.

It will be observed in the curve for the second sulfonation, that all the time between the first and third hours, equal to two hours, resulted in no change in the concentration of the acid as determined by the analyses made. This part of the curve is designated by a straight line corresponding to a concentration of

about 0.5 grams of 100% H_2SO_4 per gram of solution. In the third curve, this straight line corresponds to about a concentration of .52 grams 100% H_2SO_4 per gram of solution. The above two concentrations, within the limits of analytical error, correspond very closely to the calculations previously shown for the concentration of acid after complete mono-sulfonation is accomplished. In other words, our analytical data and theory agree that complete mono-sulfonation has been accomplished after one hours heating at or near the boiling of benzene. With this fact established, in the fourth, fifth and sixth experiments, we heated at 80° for only one hour, and analysis after this period of heating confirmed the previous results established that the mono-sulfonation is complete after this time.

As previously shown, if the di-sulfonation were complete, the final concentration of acid ought to be .223 grams 100% H_2SO_4 per gram of solution. But the concentrations obtained analytically and shown by the graphs, differ very widely from this quantity. The concentrations are for sulfonation:

No.2- .35g./c. of sol.
No.3- .31g./c. " "
No.4- .33g./c. " "
No.5- .34g./c. " "
No.6- .325g/c. " "

From the above, the conclusion is drawn that the sulfonation did not go completely to the disulfonic acid. As no means were known to make a direct quantitative test of the di-sulfonic acid actually present, we determined this percentage from the curves in the following manner:

Take the second experiment as an example. Complete sulfonation to the di-sulfonic acid corresponds to a concentration of .223 grams. Complete sulfonation to the mono-sulfonic acid corresponds to a concentration of .505 grams. Between the concentrations of .505 grams and .223 grams, the various percentages of the benzene-di-sulfonic acid are shown by the different concentrations starting with 0% di-sulfonic acid at a concentration of .505 grams and 100% di-sulfonic acid at a concentration of .223 grams. In curve #2, the concentration after complete sulfonation is .35 grams.

.505 -.223 = .282 grams or change in concentration necessary for complete sulfonation.

.505 -.35 = .155 grams or change in concentration

actually accomplished.

$\frac{.155}{.282} = 55\%$

∴ in the second, the sulfonation was only 55% complete and following this out the sodium salt would only be 55% di-sodium sulfate, the other 45% being the mono-sulfonate.

The third sulfonation was only

$\frac{.505-.31}{.505-.242} = \frac{.195}{.263} = 74\%$ complete.

The fourth sulfonation was only

$\frac{.505-.33}{.505-.258} = \frac{.175}{.247} = 71\%$ complete.

The fifth sulfonation was only

$\frac{.505-.34}{.505-.258} = \frac{.165}{.247} = 67\%$ complete.

The sixth sulfonation was only

$\frac{.505-.325}{.505-.258} = \frac{.180}{.247} = 73\%$ complete.

It can therefore be seen that the yield of resorcinol ought to be multiplied by a factor depending on the purity of the sodium salt, to determine the real efficiency of the operation.

The different efficiencies of the resorcinol yields are obtained in the following manner: The theoretical yield of resorcinol from 200 grams of benzene is 284 grams. In the second experiment, the yield was 39.8 grams. The efficiency on the ben-

zene basis is $\frac{39.8 \times 100}{284}$ or 14%. Assuming 100% sodium-benzene-di-sulfonate, the efficiency is $\frac{39.8 \times 100}{178}$ or 22.4%. But the second sulfonation was only 55% complete. ∴ the real efficiency equals $\frac{100}{55}$ x 22.4% or 40.8%. In the same manner, the different efficiencies for the other resorcinol yields were calculated and these are shown in the summary sheet.

According to Mühlhäuser (Dingl. Polyt. J. 1887,263,154) the yield of resorcinol based on 125 kilos of sodium benzene-di-sulfonate is 20 to 23 kilos and Schoop (Zeitsch. Chem. Ind. 1887,2,1) gives 30 kilos of crude resorcinol which is equivalent to 24-25 kilos of pure resorcinol, as his yield. Since 48.7 kilos is the theoretical yield from 125 kilos of sodium salt, the above figures correspond to an efficiency of 39% to 52%.

References.

From the Berichte der Deutschen Chemischen Gesellschaft, page 3162, Vol 47, III, the following is noted, "10 grams sodium-benzene-di-sulfonate were heated at 250°C for 30 hours with 6 grams NaOH in 50cc H_2O; the reaction mixture was colored a pale yellow. When acidified with H_2SO_4, sulfurous acid escaped and no trace of resorcin was obtained by extraction with ether. The solution, neutralized and run down to dryness, was extracted with alcohol; when sulfate, sulfite, and unchanged di-sulfonate salt were left behind. 45 grams of sodium-phenol-sulfonate (78% theory) were obtained from the alcoholic extract. Upon heating to 300°, only the phenol-sulfonic salt was obtained as before.

Experiment with $Ca(OH)_2$:

"From 5 grams of sodium benzene-di-sulfonate, only 3 grams of sodium-phenol sulfonate (11% theory) were obtained when the fusion was made in a mechanically agitated autoclave for 11 hours."

Dr. Paul Degener in the Journal für praktesche Chemie, Vol (2) 20, S319 in reference to the action of molten alkalies on the benzene-di-sulfonates and

and meta-phenol-sulfonate says, "This action has already been the subject of several investigations. Nölting (Berichte Berliner Chemische Gesellschaft, Vol. 8, P.1110) and Victor Meyer (Lieb. Jahresberichte 1874, S677) obtained resorcin from sodium-benzene-di-sulfonate. According to another publication, (Annalen Chemische Pharm. 174 P.235. Lieb. Jahresberichte. 1874, S676) they obtained 90-95% of the theoretical yields of resorcin thru fusion with alkali. Garrik (Zeitschrift für Chemie 1869,S.549) obtained close to the theoretical yield by heating with KOH for 2-3 hours at 230°C. Barth and Sennhofer (Berichte Berliner Chemische Gesellschaft V.9 P.972) finally proved that the fusion of m-phenol-sulfonate with KOH at 250° gave 70-80% of the theoretical yield of resorcinol free from its ortho and para isomers. The first product of the reaction is known to be the meta-phenol-sulfonate as desribed by Barth and Sennhofer. (Das. S. 969).

$$C_6H_4(SO_3K)_2 + KOH \longrightarrow C_6H_4OK\ SO_3K + KHSO_3$$

The benzene para-and meta-di-sulfonates are converted in this manner to the meta compound. (Das. S.969) It was therefore not necessary to separate the two acids

especially as these chemists stated that when the meta acid was formed by heating the benzene-monosulfonic acid with an equal weight of fuming sulfuric acid, the meta acid was almost always contaminated by only very small quantities of its isomers. . . . .

The salts of the benzene-di-sulfonic acids used in the following experiments were prepared according to the above outline and purified as much as possible by repeated crystallization. The salts were dried at 130-140°C and analyzed with the following results: .635 grams sodium benzene-di-sulfonate gave .313 grams Na_2SO_4. The theoretical amount is .318 grams. Therefore the salt was 98% pure. 1.055 grams of potassuion benzene-di-sulfonate fave 0.578 grams K_2SO_4 which is equivalent to 98.97% pure. Both of the above salts were free from alkali chlorids. . . .

In Ex. 57 and 63, the fusion mass obtained was poured into water and then treated with the calculated amount of acid. It was then exactly neutralized without further heating. The dried salts were freed as much as possible from the sulfates by crystallization and the resulting salts were extracted with alcohol in an extraction apparatus, the operation being performed

completely by several manipulations. The resorcin obtained in the remaining experiments was extracted with ether from the acidified melt, the ether was driven off and the residue was taken up with conc. HCl for a quantitative determination of the resorcinol. . . . .

These results show that that KOH is more energetic and works at a lower temperature. The NaOH generally gives smaller yields, but on lengthening the time of fusion, the difference in behavior of the two alkalies becomes less noticeable. . . .

In KOH fusion, the best yield of resorcinol is obtained between 235° and 270°. Stronger heating is destructive, especially when there is a small amount of KOH present, while with the same or a smaller amount of NaOH- if the absolute instead of the molecular weights are taken- no decomposition is noticeable. At higher temperatures and longer fusion periods, it seems unnecessary for KOH as well as NaOH fusions, to add more than 12 molecules of alkali, while a smaller mass works unfavorably."

(1st Series) Results of above Experiments.

No. of Exp.	Wt. of $C_6H_4(SO_3K)_2$	Wt. of KOH	Temp.	Time	Resorcin obtained	Meta phenol sulfonic acid obtained.
57	72 g.	255g.	170°-180°	3 hrs.		100%
58	8.45	9.6	270-280	10 min.	2.69%	-----
59	6	12.8	250-260	20 "	25.87%	-----
60	6.3	27.4	225-235	20 "	24%	-----
61	6.3	26.9	250-260	20 "	20.09%	-----
62	15.5	66.3	250-255	30 "	25.94%	--- -
63	6.3	27	270-280	20 "	21.44%	-----

Second Series.

No. of Exp.	Wt. of $C_6H_4(SO_3Na)_2$	Wt. NaOH	Temp.	Time.	Resorcin obtained	Meta phenol sulfonic acid obtained
64	64gr.	250 gr.	170-180°	2½hrs.		74.2%
65	5.2	16.1	210-218	20 min.	1.57%	----
66	8.45	6.8	245-255	20 "	14.74%	----
67	5.7	9.12	250-260	20 "	17.34%	----
68	5.7	9.12	270-280	20 "	21.11%	----
69	7.6	23.5	230-240	20 "	13.44%	----
70	5.2	16.1	225-235	20 "	13.28%	----
71	5.2	16.1	245-255	20 "	18.81%	----
72	5.2	16.1	270-280	20 "	14.04%	----

Third Series.

No. of Exp.	Wt. of $C_6H_4(SO_3Na)_2$	Wt. KOH	Wt. NaOH	Temp.	Time	Resorcin
73	5.7	6.7	4.5	250-260	20min.	20.49%
74	5.7	13.5	9.1	225-235	20 "	16.75%

Conclusions.

From the experimental data obtained from the performance of this thesis, the authors derive the following conclusions:

Sulfonation:

(1) In sulfonating, it is not necessary to heat more than 1 hour at or near the boiling point of benzene to obtain complete mono-sulfonation. Present commercial practice heats for $2\frac{1}{2}$ to 3 hours at this temperature.

(2) The fact that the sulfonation in all the experiments stop at about a concentration equal to .33 grams 100% H_2SO_4 per gram of solution, leads the authors to believe that either a higher concentration than 4% fuming acid ought to be used, or a higher temperature ought to be obtained in the latter part of the sulfonation; or both the above improvements should be utilized.

If a higher concentration of acid is used, some means to recover the excess acid, similar to the plan outlined in Dennis' patent stated before, ought to be evolved.

(3) It is apparent from the quantitative determination made that the decomposition of the H_2SO_4 during the sulfonation at 265° is negligible. If the mono-sulfonation is completed before the high temperature is reached, there will be no loss of benzene.

Conversion to the Calcium Salt:

In the conversion to the calcium salt, the lime should be thoroughly slaked for a prompt reaction and no great excess should be used; for that would add to the amount of Na_2CO_3 needed in the next operation.

Conversion to the Sodium salt:

In the conversion to the sodium salt, care must be taken that no excess is used as the Na_2CO_3 stays in the salt that is fused and this leads to bad results for the fusion operation.

Fusion:

The data made available by our experiments leads the authors to the conclusion that the best yields of resorcinol are obtained in the fusions where the higher amounts of alkalies are used at a lower temperature and longer time of fusion. To be specific, our best

results were obtained in the fifth experiment where we used $2\frac{1}{2}^{\#}$ NaOH with $1^{\#}$ sodium salt at a temperature of 280°-285° for $6\frac{1}{2}$ hours. Under the above conditions, it would be advisable to obtain some method of recovery of the free NaOH after the fusion is complete.

The conclusion to be drawn from the fact that considerable tar is formed in the fusions where a low concentration of NaOH and high temperature are maintained, is that the sodium resorcinate is first formed but is soon decomposed at the high temperature of the fusion mass and in the presence of the alkali. In our experiments, the presence of so much tar can be accounted for by the fact that the phenol formed as the result of so much mono-sulfonate, was much more susceptible to decomposition than the resorcinol.

Neutralization:

In acidifying, the acid should be added from the bottom of the solution, which absorbs the SO_2 and thus cuts down the amount of acid actually required. No excess of the acid should be used as it forms the hydrochlorid with the resorcinol.

Preparation of the Dried Salts:

A better and quicker extraction of resorcinol from the dried salts is accomplished by having the salts ground fine.

Extraction:

From our observations and work, it is self-evident that alcohol is a very desirable solvent to be used for the extraction of the resorcinol from the salts. Its adaptability, ease of handling, cost, and efficient recovery, make it most admirable for this use.

Resorcinol Purification:

To our minds, the most efficient manner that this can be accomplished is by means of a vacuum distillation. Ordinarily resorcinol boils at 276.5°C. With a good vacuum it comes over at 150°C. This does away with the necessity for a high temperature and as a consequence, no decomposition of the resorcinol occurs.